

A Tunable Dendritic Molecular Actuator

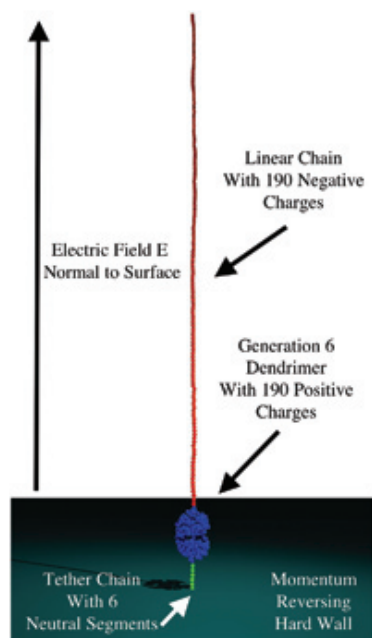
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Molecular devices for applying strains or forces on demand play a central role in many envisioned nanomachines. Thus, there are a number of such actuators proposed in the literature [1]. Many rely upon local conformational changes in their chemical constituents that translate into relatively small but rapidly applied strains or are best described as two-state rotors. Typical polymeric actuators display percent strains in the 3–30% range. If we are to mimic biological processes, however, large strains will also be of interest. For example, the actomyosin complex produces displacements in the range of 5–10 nm [2]. Global conformational changes in linear polymers offer one route to achieve such large-scale motions. Electrostatic attraction seems an obvious choice to effect these conformational changes since the force generated can be quite high and the presence of charges permits coupling of the device to an external electric field. Here, I present a

construction designed to mimic a spring-loaded reel, with a linear chain serving as the molecular analog of a string that is pulled onto a dendritic molecular spool. Electrostatic attraction serves as the spring while an applied electric field allows the compliance to be tuned.

Through Brownian dynamics simulations, I studied a model rendition of the proposed device based on a sixth generation monocentric dendrimer, such as monocentric dendritic-poly(propylenimine), with charges at every branch point and terminal group. A noncharged, short tether chain is grown from one of the dendrimer's terminal groups and is immobilized at the chain end on a hard-wall surface. From another terminal group, topologically opposed to the growth point of the tether, another linear chain is attached. This chain is oppositely charged to the dendrimer and has the same number of charged groups as the dendrimer so that the overall system is charge-neutral. An electric field E was applied normal to the surface and acts to pull the chain away from the surface and the dendrimer toward it, except in the one instance noted below in which the field polarity was reversed. This contributes an additional force of magnitude $|Eq|$ to each of the charges of magnitude q along the axis normal to the surface. See Fig. 1.

Fig. 1.
The model molecular actuator.



The equilibrium free energy as a function of the distance from the chain end to the center of the dendrimer was determined via the Jarzynski [3] identity. To accomplish this, a phantom spring was attached to the free chain end and retracted at a constant rate normal to the surface. Information (instantaneous retractive force, etc.) from numerous simulations was combined after the method of Hummer and Szabo [4] to reconstruct the free energy profiles.

Figure 2 illustrates the location of the minima of the free energy as a function of applied field strength for the case of a high solution salt concentration. The equilibrium displacement X_e remains constant until a critical field strength E^*

is applied, after which there is a rapid rise in the value of X_e . Qualitatively, this indicates that the device undergoes a phase transition similar to that of an Ising magnet in an applied field since the susceptibility dX_e/dE appears to diverge at the critical field strength E^* . The displacement X_e serves as the order parameter analogous to the magnetization in the Ising magnet, and there is a one-to-one correspondence between the applied fields in both models. The critical field strength E^* is expected to shift to higher values with decreasing solution salt concentration; the less salt in the system, the more tightly bound is the chain to the dendrimer and, thus, more energy is required to separate them. This was observed to hold for the model studied here.

Finally, the retractive force F exerted on an attached object may be tuned by cycling the electric field, as shown in Fig. 3. A typical conformation was chosen from an ensemble of equilibrated actuator in a high salt solution and an electric field strength well above the critical value. An immobile phantom spring was attached to the chain end. The first plateau represents the time during which the field was on. The slight positive force exerted by the device results because a configuration with displacement slightly less than X_e was chosen. When the field is turned off, the actuator quickly retracts, exerting a force on the phantom spring. The field is then cycled on again returning the retractive force to its original value. Thus, the actuator displays a lack of hysteresis as expected since no entanglement is observed between the linear and branched segments in this model. This is consistent with rheological studies of blends of hyperbranched and linear chains. The final plateau with a stronger retraction on the phantom spring results when the field polarity is reversed, effectively driving the dendritic and linear portions

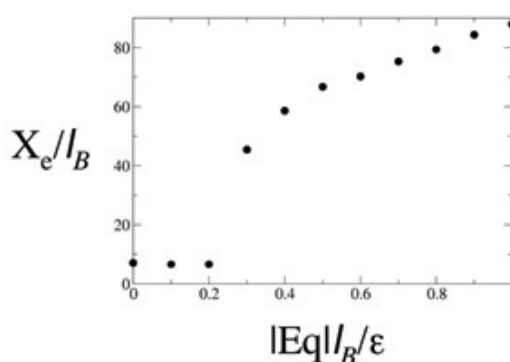


Fig. 2. The equilibrium distance X_e between the center of the dendrimer and the end of the charged chain as a function of the applied field E . Dimensions of length and energy are given in units of the Bjerrum length l_B and the Lennard-Jones prefactor ϵ , respectively.

of the construct together. More details of this study may be found in Ref. [5].

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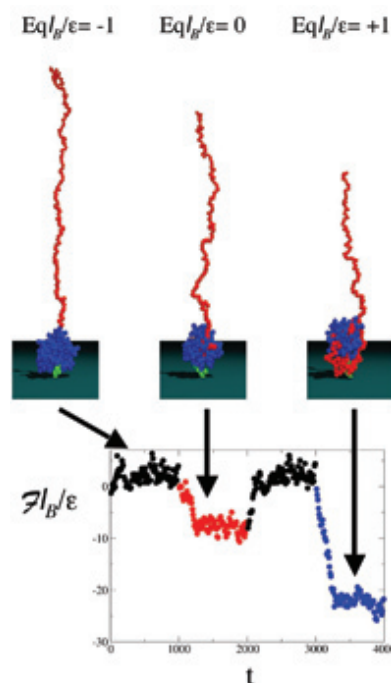


Fig. 3. The retractive force F of the extended actuator as a function of time t and typical snapshots for each condition are shown.